Eastern University, Sri Lanka

Third Examination in Science

Special Degree in Chemistry-2011/2012(2016)

CHS01-Inorganic Chemistry-I

Answer all questions   **Time: Two hours**

a) With or without the aid of a flow chart, identify the point groups of the following molecules.

   i) ethane (staggered)

   ii) SiH_3I

   iii) *fac*-$Co(NH_3)_3Cl_3$

   iv) I_3^- (liner)

   (20 marks)

b) "Symmetry operation C_2 commutes with Symmetry operation σ_v for H_2O molecule" Explain this statement.

   (20 marks)

c) What are the symmetry operations in the point group C_{3v}? Identify a molecule that belongs to this group. By examining the effect of sequential application of the various symmetry operations in the group, construct the group multiplication table for the point group C_{3v}.

   (20 marks)

Contd...

d) i) Define the term "irreducible representations (IRs)"

ii) The following is the charter table for Td point group.

T$_d$	E	8C$_3$	3C$_2$	6S$_4$	6σ_d	linear functions, rotations	quadratic functions
A$_1$	+1	+1	+1	+1	+1	-	$x^2+y^2+z^2$
A$_2$	+1	+1	+1	-1	-1	-	-
E	+2	-1	+2	0	0	-	$(2z^2-x^2-y^2, x^2-y^2)$
T$_1$	+3	0	-1	+1	-1	(R_x, R_y, R_z)	-
T$_2$	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)
Γ_R	7	1	3	-1	1		

I) Write down the meaning of all the symbols seen in column 1 (under Td)

II) Decompose the reducible representation Γ_R into irreducible representations using the relevant formula.

(40 ma

2 a) Briefly explain the following;

i) Russel-Saunders coupling

ii) Hund's rules to determine the ground state term of a free ion

(40 mar

b) Determine the Russell-Saunders ground state term for each of the following ions

i) Ti^{3+} ii) Cu^{2+} iii) Ni^{2+}

(30 mar

c) Write the term symbols (Russell-Saunders coupling) for the electron configuration: 2s^1

(30 mar

3 a) What is Orgel energy diagram? Draw the combined Orgel energy level diagram for d^3 configuration in octahedral and tetrahedral field.

(30 marks)

b) Answer the following questions about electronic spectroscopy of the transition metal complexes.

i) Explain why the *Laporte* selection rule is often relaxed (partially violated) in real complexes.

ii) Explain why the molar absorptivity of the peaks in the absorption bands in the visible region of $[Co(H_2O)_6]^{2+}$ is 10 L mol^{-1} cm^{-1} while that for $[CoCl_4]^{2-}$ is 600 L mol^{-1} cm^{-1}.

(40 marks)

c) What do you understand by the term, *Jahn-Teller* distortion? Explain the z-out and z-in phenomena with examples

(30 marks)

4 a) Consider the electronic structure of the complexes $[Fe(CN)_6]^{4-}$ and $[Fe(OH_2)_6]^{2+}$ to answer the following (*Note*: you should use Tanabe-Sugano diagram provided at the end of this exam paper)

i) What is the ground term for $[Fe(CN)_6]^{4-}$ and for $[Fe(OH_2)_6]^{2+}$

ii) Which transitions are spin allowed for $[Fe(CN)_6]^{4-}$ and for $[Fe(OH_2)_6]^{2+}$.

(40 marks)

b) Briefly explain the "Symbiotic theory for linkage isomers"

(20 marks)

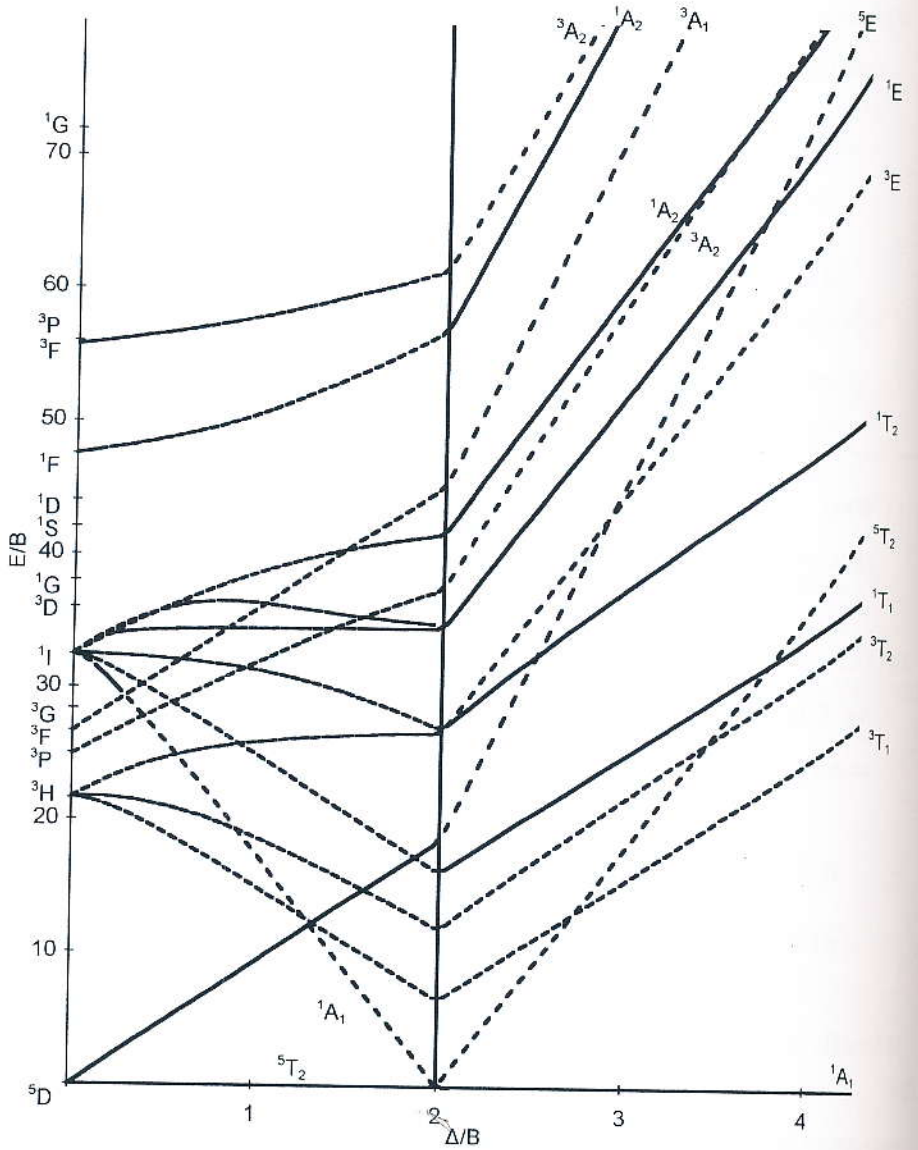c) Explain how the following factors influence the structure determination of linkage isomers

i) Effect of π-bonding

ii) Steric effects on linkage isomers

(40 marks)

Contd...

Tanabe-Sugano diagram (d⁶)

End of paper